

Crystal and Molecular Structure of 3-Methylpyridine-Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)lutetium(III)

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The crystal structure of 3-methylpyridine-tris(2,2,6,6-tetramethyl-3,5-heptanedionato)lutetium(III), Lu(C₁₁H₁₉O₂)₃·C₆H₇N, has been determined from 6385 independent intensities measured by counter methods. The crystal system is monoclinic with $a = 17.404$ (3), $b = 10.118$ (2), $c = 24.268$ (4) Å, and $\beta = 96.31$ (5)^o, and the space group is $P2_1/c$. There are four molecules per unit cell. Least-squares refinements lead to a residual of 0.079. The lutetium ion is seven-coordinate, with the six oxygen atoms of the three diketo groups and the nitrogen atom of the 3-methylpyridine molecule occupying the vertices of a capped trigonal prism. There is no intermolecular hydrogen bonding.

Introduction

Certain paramagnetic lanthanide complexes of the anion of 2,2,6,6-tetramethylheptane-3,5-dione, (CH₃)₃-CCOCHCOC(CH₃)₃, or C₁₁H₁₉O₂⁻ produce large shifts in the nmr spectra of some molecules in solution. The first shift reagent discovered was the bis(pyridine) adduct Eu(C₁₁H₁₉O₂)₃·2C₅H₅N,¹ and it was soon shown that Eu(C₁₁H₁₉O₂)₃ itself was an even better shift reagent.² The mechanism by which these reagents produce nmr shifts has been the subject of widespread interest and speculation, and explanations have tended toward either contact or pseudocontact interactions, or a combination of these.

Quantitative interpretation of the shifts requires stereochemical information on the adducts, and the crystal structures of selected shift reagents and related compounds can provide some of the essential geometric knowledge. Horrocks, Sipe, and Lubert³ have determined the crystal structure of the eight-coordinate bis(4-methylpyridine) adduct Ho(C₁₁H₁₉O₂)₃·2C₆H₇N and Cramer and Seff⁴ have reported the structure of Hinckley's original shift reagent,¹ Eu(C₁₁H₁₉O₂)₃·2C₅H₅N, which is also eight-coordinate. These structure determinations have shown that assumptions of axial symmetry are invalid for these complexes. The necessity for such assumptions may be obviated by means of a set of reasonably accurate interatomic distances, from which the shifted spectrum may be calculated; such calculations were carried out by Cramer and Seff for Eu(C₁₁H₁₉O₂)₃·2C₅H₅N.⁵

Our original intention was to determine the crystal structure of the 3-methylpyridine adduct Yb(C₁₁H₁₉O₂)₃·C₆H₇N. Due to problems with stability, work was shifted to the isomorphous diamagnetic lutetium compound Lu(C₁₁H₁₉O₂)₃·C₆H₇N.

Experimental Section

The compounds were prepared and purified by Tincher⁶ following the method of Eisentraut and Sievers⁷ for obtaining the Ln(C₁₁H₁₉O₂)₃ chelates and the method used by Hinckley¹ for forming adducts in which crystals were grown from a solution of the Ln(C₁₁H₁₉O₂)₃ complex in the solvating liquid. Crystals were also obtained by adding an excess of 3-picoline to a solution of the

chelate in *n*-hexane. Analytical results given by Tincher⁶ confirm the Ln(C₁₁H₁₉O₂)₃·C₆H₇N stoichiometry.

A crystal of Lu(C₁₁H₁₉O₂)₃·C₆H₇N of dimensions 0.55 × 0.23 × 0.12 mm was sealed in a glass capillary. Weissenberg and precession photographs showed monoclinic symmetry, and the space group suggested by systematic absences was $P2_1/c$; this space group was ultimately confirmed by the structure. Accurate cell dimensions were obtained on a General Electric XRD X-ray spectrometer equipped with a single-crystal orienter. Using Cu K α radiation (λ 1.5418 Å), the dimensions are $a = 17.404$ (3), $b = 10.118$ (2), $c = 24.268$ (4) Å, and $\beta = 96.31$ (5)^o. The density calculated on the basis of 4 molecules per unit cell is 1.279 g/cm³; the density measured by flotation is 1.28 g/cm³.

Diffracted intensities were measured on a Philips Paired diffractometer using Mo K α radiation reflected from a silicon monochromator. The Paired operates on Weissenberg geometry, and the layers from $k = 0$ to $k = 12$ were measured with a maximum $(\sin \theta)/\lambda$ of about 0.62. For each reflection an ω scan was carried out at the rate of 1.0^o/min. Scan ranges varied from 1.4^o (0.7^o on each side of the peak) on the zeroth layer to 4.4^o for the low-angle reflections on the twelfth layer. The data were corrected for intensity fluctuations and crystal deterioration by monitoring standard reflections on each layer and the 400 reflection as an overall standard. An intensity variation of 23% occurred over the 3 weeks required for data collection. Background counts were collected for 20 sec at each end of the scan. The background corrections were obtained by fitting these counts, for the unobserved reflections only, to the equation $1/B = C + Ds^2 + Es^4$, where B is the background, s is $(\sin \theta)/\lambda$, and C , D , and E are constants.

After correction for fluctuations and background, the Lorentz-polarization factor was applied,⁸ and a value of F was obtained for each reflection. This F was accompanied by a standard deviation, σ , which included all effects of counting errors on intensity measurements and corrections for fluctuations and background. Reflections for which F was less than σ were regarded as unobserved and were omitted from subsequent calculations. Of the 8611 reflections measured, 6629 were observed, and combining reflections that had been measured more than once left 6385 independent observed values of F . These data were corrected for absorption by means of an adaptation of the program of Burnham.⁹ The value of the linear absorption coefficient is 24.82 cm⁻¹, and the transmission coefficient varied from 0.576 to 0.754. A set of adjusted standard deviations was computed from $(\sigma^2 + 0.0004F^2)^{1/2}$.

Structure Determination and Refinement

The lutetium positions were deduced from the three-dimensional Patterson function. These atoms occupy general positions of space group $P2_1/c$, $\pm(x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z)$, with $x = 0.277$, $y = 0.107$, $z = 0.176$. All Fourier and refinement calculations were carried out with the X-Ray System 1970 of programs.¹⁰

(8) L. D. Jennings, *Acta Crystallogr., Sect. A*, 24, 472 (1968); P. Suortti and T. Paakkari, *J. Appl. Crystallogr.*, 1, 121 (1968).

(9) C. W. Burnham, "World List of Crystallographic Computer Programs," International Union of Crystallography, Groningen, 1962, Program 338.

(10) Relevant programs of the X-Ray System 1970, J. M. Stewart, Ed., University of Maryland, College Park, Md., include the Fourier program FOURR, the general least-squares refinement program CRYLSQ, the bond lengths and angles program BONDLA, and the structure factor table preparation program LIST FC.

(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, 91, 5160 (1969).

(2) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

(3) W. DeW. Horrocks, Jr., J. P. Sipe, III, and J. R. Lubert, *J. Amer. Chem. Soc.*, 93, 5258 (1971).

(4) R. E. Cramer and K. Seff, *Chem. Commun.*, 400 (1972).

(5) K. Seff, personal communication.

(6) G. L. Tincher, M.S. Thesis, University of Kentucky, Lexington, Ky., 1970.

(7) K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, 87, 5254 (1965); *J. Inorg. Nucl. Chem.*, 29, 1931 (1967).

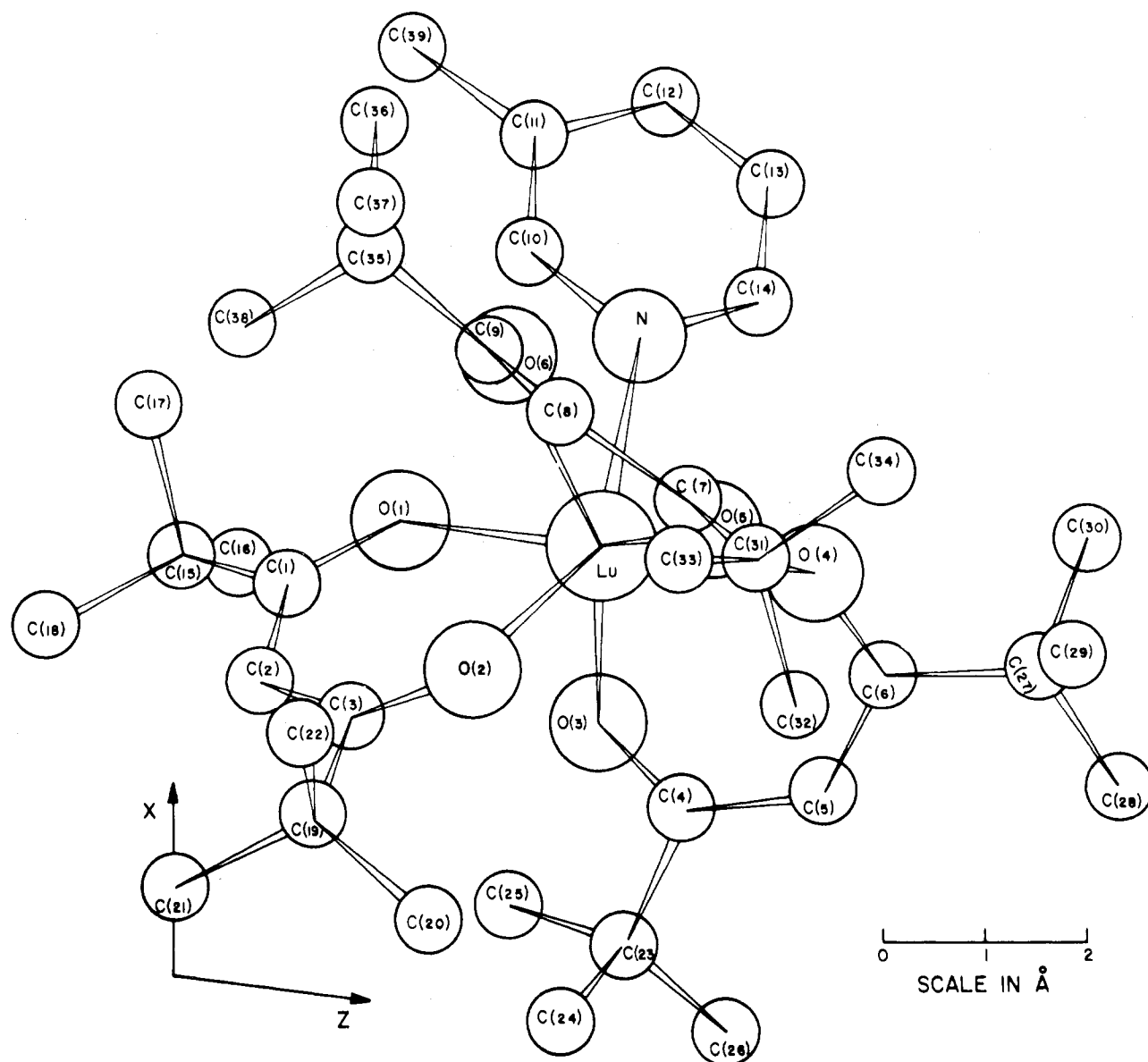


Figure 1. One molecule of $\text{Lu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot \text{C}_6\text{H}_7\text{N}$ projected onto (010).

Successive Fourier and least-squares calculations yielded the positions of the carbon, oxygen, and nitrogen atoms.

Full-matrix, least-squares refinements were carried out refining one scale factor, positional coordinates for one lutetium atom, 39 carbon atoms, six oxygen atoms, and one nitrogen atom, isotropic temperature factors for 36 carbon atoms, six oxygen atoms, and one nitrogen atom, and anisotropic temperature factors for the lutetium atom and three of the carbon atoms. The three carbon atoms selected for the anisotropic treatment were methyl carbons of one *tert*-butyl group that seemed to be undergoing a large amount of motion as manifested by isotropic temperature factors of approximately 15. Atomic scattering factors for the neutral atoms and anomalous dispersion corrections for the lutetium atom were taken from the compilation in ref 11. The quantity minimized in the refinements was $\sum w(|F_o| - |F_c|)^2$, in which the weight w was $1/\sigma^2$, and σ was the adjusted standard deviation described above. At the end of the refinements the residual $R = \sum |F_o - F_c| / \sum |F_o|$ was 0.079, and $\sum w|F_o - F_c| / \sum w|F_o|$ was 0.073. The standard deviation of an observation of unit weight, $[\sum w(F_o - F_c)^2 / (n - m)]^{1/2}$, where n is the number of observations (6385) and m is the number of variables refined (209), was 2.08. The average ratio of shift to standard deviation in positional parameters was 1.22, and the largest value was 6.90 for one

of the parameters of the carbon atoms with great thermal motion. Hydrogen atom positions were not determined.

The observed and calculated structure factors are available.¹² The atomic positions and temperature factors are listed in Table I.

Discussion

The $\text{Lu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot \text{C}_6\text{H}_7\text{N}$ molecule is shown in Figure 1 projected onto (010). The bond lengths and angles are given in Table II. The seven-coordinate lutetium atom is bonded to the six oxygen atoms of the diketo ligands and to the nitrogen atom of the 3-methylpyridine molecule. The average Lu-O bond distance is 2.238 Å, in good agreement with the 2.243-Å distance predicted by the empirical relationship of Lingafelter and Braun¹³ for acetylacetonate complexes if an ionic radius of 0.85 Å is used for Lu^{3+} .

(12) A listing of structure factor tables will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-187.

(13) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

(11) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

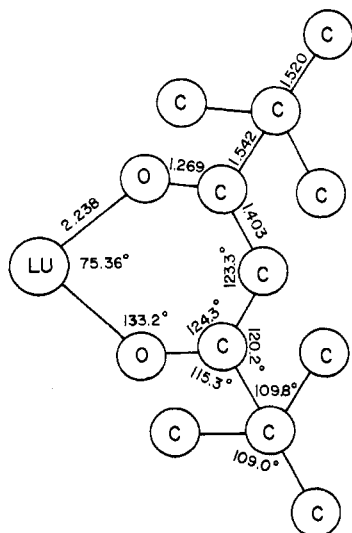


Figure 3. Average dimensions of a ring in $\text{Lu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot \text{C}_6\text{H}_7\text{N}$.

also occurs in eight-coordinate species, and Ho-N is 0.26 Å greater than Ho-O in $\text{Ho}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot 2\text{C}_6\text{H}_7\text{N}$,³ and Eu-N is 0.30 Å greater than Eu-O in $\text{Eu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot 2\text{C}_5\text{H}_5\text{N}$.⁴

The average intraring O-O distance, the "bite" of the chelate ring, is 2.74 Å, as compared with 2.74 Å for $\text{Dy}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3\text{H}_2\text{O}$,¹⁹ 2.83 Å for $\text{Pr}_2(\text{C}_{11}\text{H}_{19}\text{O}_2)_6$,²⁰ 2.71 Å for $\text{Ho}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot 2\text{C}_6\text{H}_7\text{N}$,³ and 2.74 Å for $\text{Eu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot 2\text{C}_5\text{H}_5\text{N}$.⁴

The mean dimensions of the chelated ligand are shown in Figure 3. The five atoms O-C-C-C-O in each ring are quite planar, with root-mean-square deviations from the least-squares planes of 0.006, 0.017, and 0.019 Å, respectively, for the planes O(1)-C(1)-C(2)-C(3)-O(2), O(3)-C(4)-C(5)-C(6)-O(4), and O(5)-C(7)-C(8)-C(9)-O(6). The distances of the lutetium atom from these mean planes are 0.236, 0.470, and 0.827 Å; these bendings of the chelate rings are rather typical.^{14,16,17,21}

The root-mean-square deviations of the six atoms N, C(10), C(11), C(12), C(13), and C(14) from their least-squares plane is 0.011 Å, and the methyl carbon atom, C(39), is

(21) J. A. Cunningham, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **6**, 499 (1967); T. Phillips, II, D. E. Sands, and W. F. Wagner, *ibid.*, **7**, 2295 (1968).

0.072 Å away. The lutetium atom is only 0.003 Å from this plane.

There are no O-O intermolecular contacts less than 4.0 Å, and the shortest intermolecular distance involving C, O, and N atoms is 3.55 Å. There is thus no hydrogen bonding present, in contrast to many other chelates in which hydrogen bonding is an important structural feature.^{14,16,17,21} On the basis of their study of the $\text{Pr}_2(\text{C}_{11}\text{H}_{19}\text{O}_2)_6$ structure, Erasmus and Boeyens²⁰ concluded that seven-coordination would be impossible if the metal-oxygen distances were below 2.27 Å. Their subsequent discovery that $\text{Dy}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3\text{H}_2\text{O}$ was seven-coordinate was explained by invoking hydrogen bonding,¹⁹ and this might also be used to explain the seven-coordinate ytterbium acetylacetonate complexes.^{14,16} However, the complete lack of intermolecular hydrogen bonding in the present case robs their suggestion of its predictive power.

Although nmr shifts induced in a number of compounds by $\text{Pr}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$, $\text{Eu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$, and $\text{Yb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ have been measured,²² data have not been reported for 3-methylpyridine. We hope to undertake these measurements on $\text{Yb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot \text{C}_6\text{H}_7\text{N}$ if suitable stable solutions can be prepared. The availability of these experimental results will provide incentive for attempting to calculate the proton magnetic resonance shifts. The low molecular symmetry of this compound leaves the direction of the magnetic axis completely unknown and, although some obvious trial axes exist (e.g., Yb-N or Yb-O(1)), a trial-and-error or iterative computational procedure would be necessary. The lack of axial symmetry in these shift reagent adducts has been noted before and has been demonstrated by magnetic anisotropy measurements as well as by crystal structure data.²³

Registry No. $\text{Lu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot \text{C}_6\text{H}_7\text{N}$, 36813-01-1.

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(22) J. Reuben and J. S. Leigh, Jr., *J. Amer. Chem. Soc.*, **94**, 2789 (1972); C. Beute, Z. W. Wolkowski, and N. Thoai, *Tetrahedron Lett.*, 817 (1971); *Chem. Commun.*, 700 (1971); Z. W. Wolkowski, *Tetrahedron Lett.*, 821, 825 (1971).

(23) W. DeW. Horrocks, Jr., and J. P. Sipe, Abstract of Paper 5.1, 13th Experimental NMR Conference, Asilomar, Calif., April 1972.